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## **First Annual Technical Report**

### **Cornell Program for the Design and Synthesis of Advanced Materials**

**May 1, 1993 - April 30, 1994**

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**Submitted by:**

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## I Overview

An AFOSR-URI Program for the Design and Synthesis of Advanced Materials was established at Cornell University in May 1993, with the goal of bringing together faculty working in materials science, chemistry and mechanics. The funding from the AFOSR was used for two purposes; supporting the research of graduate students working on projects that are focussed on advanced materials and developing specialized research facilities critical for these projects, including a Processing Laboratory, a Mechanical Testing Laboratory and two workstations. The faculty supported by the Program includes Dieckmann, Giannelis, Nichols and Sass in the Department of Materials Science and Engineering; Hui, Phoenix and Zehnder in the Department of Theoretical and Applied Mechanics; and Burlitch in the Department of Chemistry. The initial challenge faced by the Program was to bring together the three rather disparate disciplines of materials science, chemistry and mechanics, with their different technical languages, and facilitate their focusing on solving a common problem. To overcome this challenge, during the past year all the faculty and students supported by the AFOSR grant met for monthly seminars to hear presentations on past work, the latest results and future plans.

Fig. 1 is a flow diagram which summarizes the philosophy of the Program. Briefly, metal-ceramic and ceramic-ceramic microstructures will be produced by a variety of innovative *in situ* processing techniques summarized in the upper portion of Fig. 2. Then, testing will be performed to evaluate the mechanical properties for correlation with the microstructures as a means of searching for optimum properties. Mechanics modelling will be performed to calculate the mechanical properties associated with the microstructures, as outlined in the lower portion of Fig. 2. Finally, after checking the validity of the predictions of the mechanics calculation by comparison with the experimental measurements of the mechanical properties, the theoretical models will be used to predict microstructures, e.g. size, morphology and distribution of the metallic and ceramic phases, that give optimum mechanical properties. These desirable microstructures will then be synthesized.

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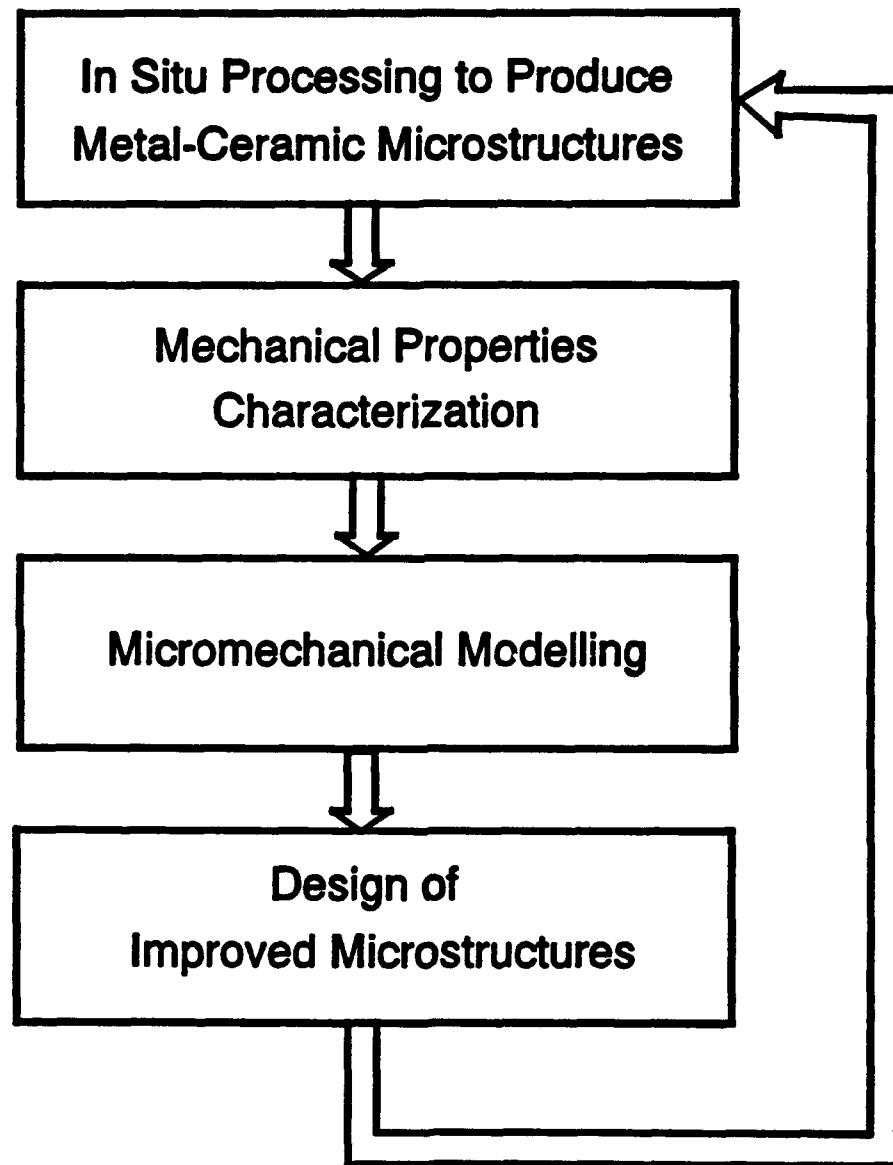


Figure 1 Flow diagram illustrating the philosophy of the Cornell AFOSR/URI.

## In Situ Processing of Metal-Ceramic Microstructures

*Materials Science; Chemistry*

- Reduction reactions
- Displacement reactions
- Molecular and nano-scale processing
- Intercalation of layered solids

## Micromechanical Modelling

*Mechanics*

- Effect of volume fraction of metal particles on thermal stresses
- Critical metal particle size when mismatch in thermal expansion coefficient
- Fracture toughness of complex metal-ceramic microstructures

Figure 2 Details of the *in situ* and micromechanical modelling components of the Cornell AFOSR/URI.

## II. Progress Report

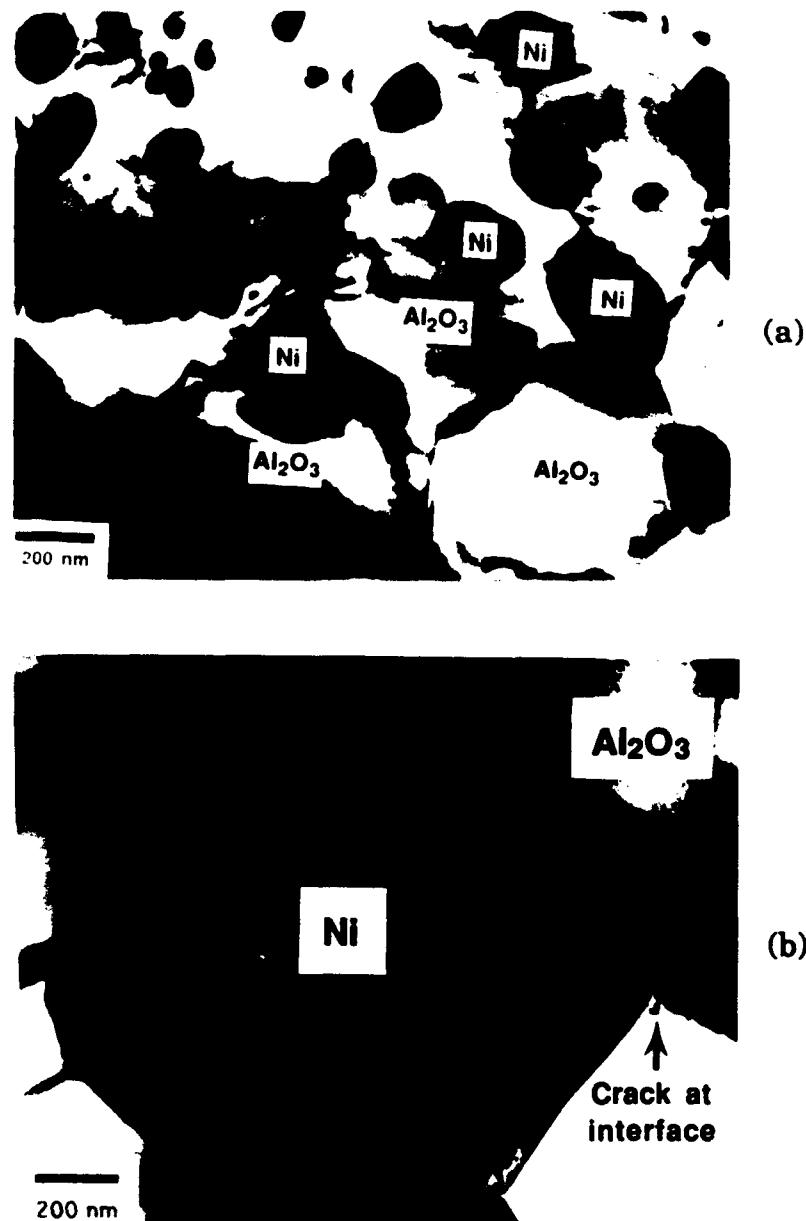
### A. Research Results

#### 1. *In Situ* Processing

It is well recognized that the fracture toughness of brittle ceramic materials can be increased by the addition of a dispersed second phase such as a ductile metal. The metallic phase can be either continuous or in the form of particulates homogeneously dispersed in the ceramic matrix. Burlitch, Dieckmann, Giannelis and Sass are working on a variety of *in situ* processing techniques to produce metal-ceramic and ceramic-ceramic microstructures with improved fracture resistance with respect to a pure ceramic.

Sass is using partial reduction reactions to produce metal-ceramic microstructures in the Ni-Al-O system, starting with the spinel phase  $\text{NiAl}_2\text{O}_4$ . Fig. 3(a) shows the typical  $\text{Ni}-\text{Al}_2\text{O}_3$  microstructure formed at high temperatures ( $1350^\circ\text{C}$ ). Surprisingly, the  $\text{Ni}-\text{Al}_2\text{O}_3$  interface survives cooling from high temperatures, though there is large thermal expansion coefficient mismatch between the Ni and  $\text{Al}_2\text{O}_3$ . Additional observations in Fig. 3(b) indicate that there is a critical size above which cracks begin appearing at the metal-ceramic interface. Sass and Hui are collaborating on a theoretical calculation of the critical particle size, described below, which will be used as the basis of controlling microstructures to avoid interface cracking. Reduction reactions at lower temperatures ( $1100^\circ\text{C}$ ) produce long rods of Ni in a defect (Ni-poor) spinel matrix. (Fig. 4 (a,b)) The defect spinel is a metastable phase with a nearly cubic structure.

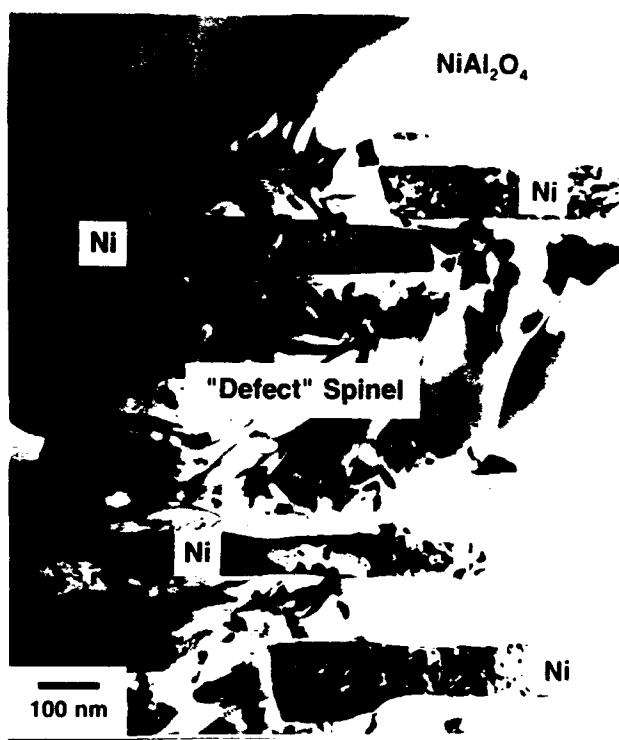
The large volume change associated with the removal of oxygen during the formation of Ni and  $\text{Al}_2\text{O}_3$ , ~19%, gives rise to cracking along the original spinel grain boundaries, as shown in Fig. 5 (a). The addition of 10 wt. pct.  $\text{ZrO}_2$  was shown to suppress this cracking, as illustrated in Fig. 5 (b). As little as 2.5 wt. pct.  $\text{ZrO}_2$  would also have a similar effect. The origin of this beneficial effect is not known at present, though it is seen that the grain size is typically 1 - 2  $\mu\text{m}$  after the addition of  $\text{ZrO}_2$ , as compared to greater than 50  $\mu\text{m}$  in the undoped  $\text{NiAl}_2\text{O}_4$ ,



**Figure 3** Microstructures produced by reduction reactions starting with  $\text{NiAl}_2\text{O}_4$ .  
(a) 1/2 hours at 1350°C. (b) 8 hours at 1300°C



(a)



(b)

**Figure 4** Microstructures produced by reduction reactions at 1100°C for 2 hours, starting with  $\text{NiAl}_2\text{O}_4$ . (a) Scanning electron micrograph. (b) Transmission electron micrograph.

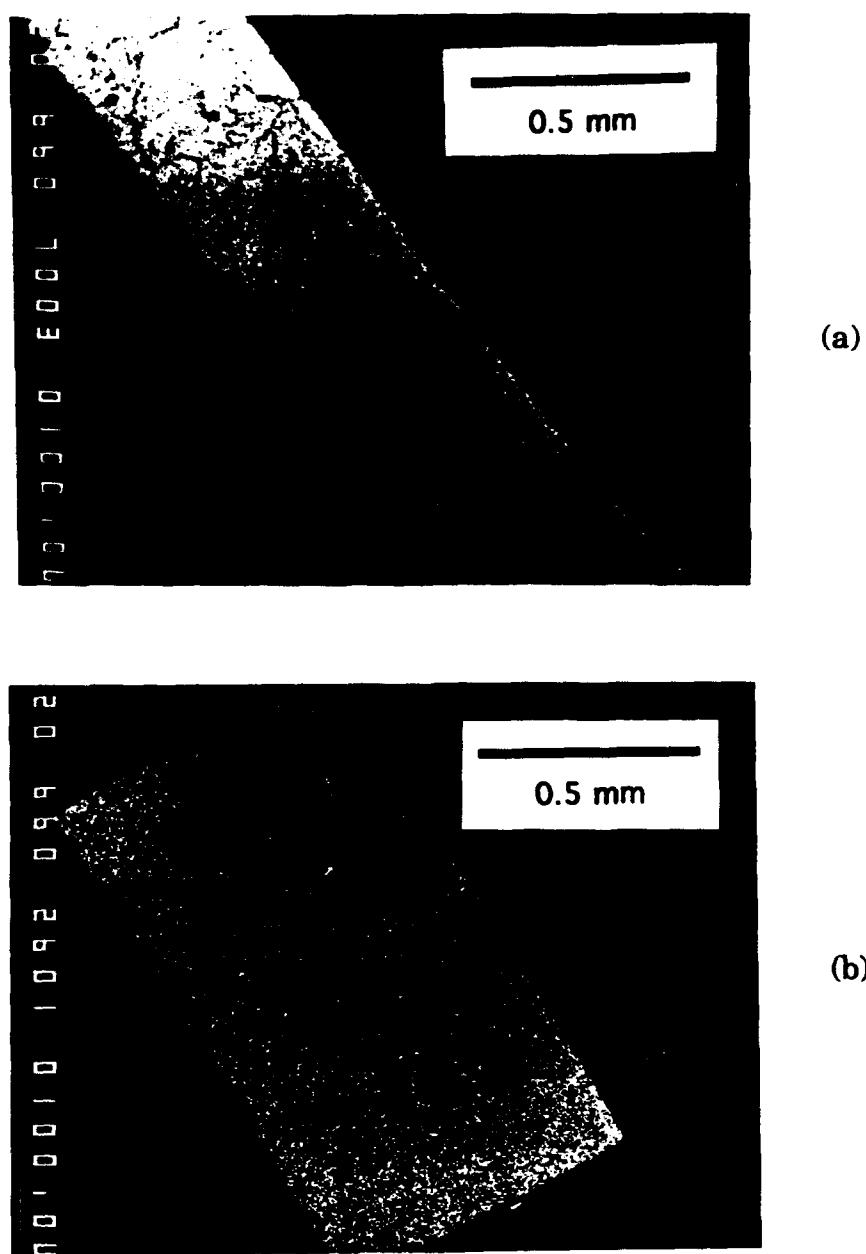


Figure 5 (a)  $\text{NiAl}_2\text{O}_4$  reduced at  $1300^\circ\text{C}$ . (b)  $\text{NiAl}_2\text{O}_4$  reduced at  $1300^\circ\text{C}$  with 10 wt. pct.  $\text{ZrO}_2$ .

suggesting that enhanced transport along grain boundaries may play a role in avoiding cracking during reduction.

With the goal of forming ceramic-ceramic microstructures with useful high temperature properties, Sass carried out precipitation reactions in the Ni-Al-O system starting with the spinel phase, to form ceramic second phase particles in a ceramic matrix. Depending on the heat treatment conditions the second phase was either a Ni-poor defect spinel or equilibrium  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

Preliminary fracture toughness measures using indentation techniques indicated that the second phase particles did not enhance the fracture of the two phase mixture over that of the starting spinel phase.

Dieckmann is working to establish an understanding of the reactions involved in the *in situ* fabrication of metal-ceramic microstructures in the Ni-Al-O system, including (i) partial reduction reactions of NiAl<sub>2</sub>O<sub>4</sub>, (ii) displacement reactions between liquid Al and solid NiO, and (iii) displacement reactions between liquid Al and NiAl<sub>2</sub>O<sub>4</sub>. He has succeeded in growing single crystals of NiAl<sub>2</sub>O<sub>4</sub> and NiO by the floating zone method in an oxygen atmosphere using a halogen lamp in a single ellipsoid image furnace. Fig. 6 shows a NiAl<sub>2</sub>O<sub>4</sub> single crystal grown at a rate of 5 mm/h with a rotation rate of 30 rpm and in an oxygen atmosphere. Both types of single crystals will be used for studies of the kinetics of reactions involved in the *in situ* formation of metal-ceramic microstructures in the Ni-Al-O system.

Dieckmann has obtained early results for displacement reactions between NiO and liquid Al. He has observed that the reaction products include a spinel phase, and Al<sub>2</sub>O<sub>3</sub> and an Al matrix, with Al-rich intermetallic phases dispersed in them. The reaction between solid Al and NiO occurs very slowly and is therefore not useful for the *in situ* fabrication of metal-ceramic microstructures in the Ni-Al-O system with reasonable processing times.

Dieckmann has also studied displacement reactions between NiAl<sub>2</sub>O<sub>4</sub> and Al as a means of circumventing the problem of cracking introduced during partial reduction reactions. This may be an alternative process to produce large

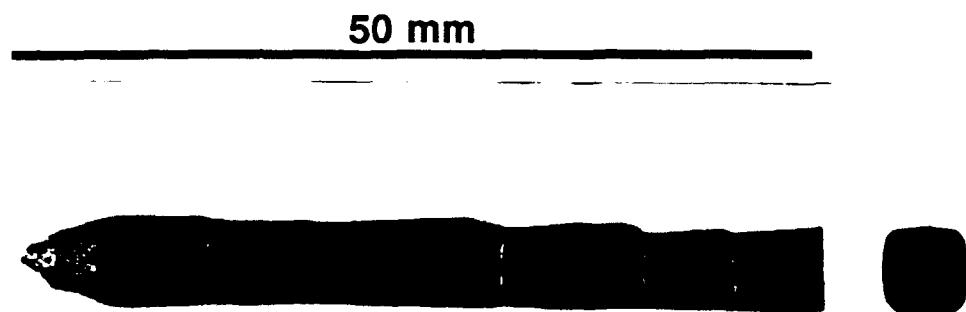


Fig. 6 NiAl<sub>2</sub>O<sub>4</sub> single crystal

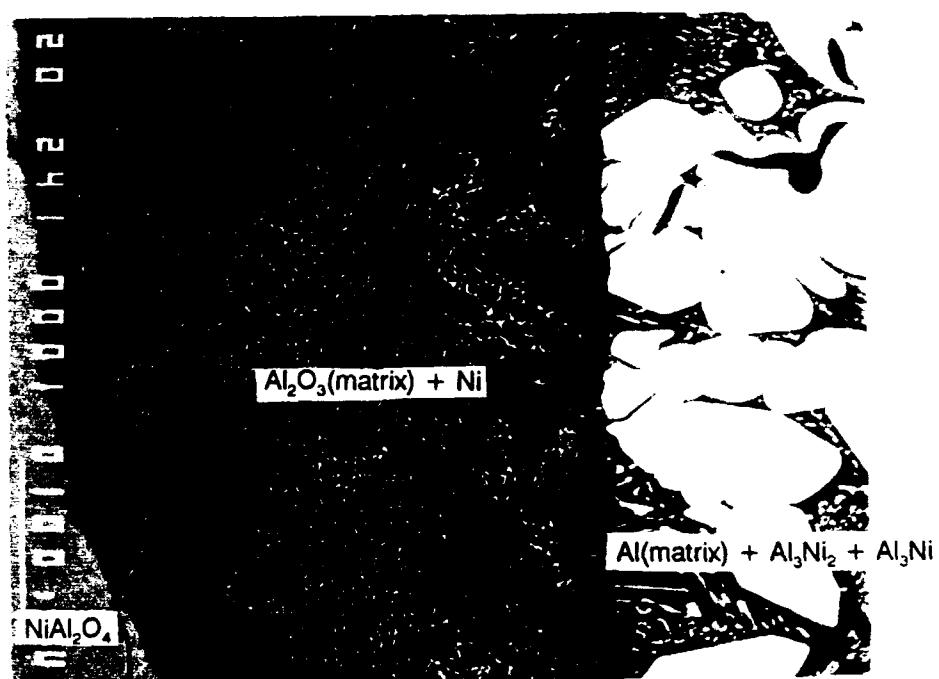


Fig. 7 Illustrating the microstructures produced by a displacement reaction between Al and NiAl<sub>2</sub>O<sub>4</sub> at 1200°C for 2 hours.

samples overcoming the problem of long range diffusion for the formation of the metal-ceramic microstructures. Initial results from the reaction between liquid Al and NiAl<sub>2</sub>O<sub>4</sub> at 1200°C for 2 hours show an unreacted spinel layer, Al-rich finger-like features, within a two-phase area of Ni and Al<sub>2</sub>O<sub>3</sub>, and an Al-rich layer with intermetallic phases dispersed in them (See Fig. 7).

A microstructure with an interpenetrating (bicontinuous) ceramic and metal network might offer some unique mechanical properties, since the continuous metal and ceramic phases could lead to improved fracture toughness and creep resistance, respectively. Typically metal-ceramic composites (often called cermets) have been produced by dry mixing of ceramic and metal powders followed by hot pressing or sintering. This process is often difficult to control, resulting in nonuniform dispersion of the components. In contrast, chemical techniques offer several advantages compared to traditional powder processing techniques, such as greater control over stoichiometry and microstructure. In addition, chemical techniques have the advantage of simplicity and low cost, and they are readily scaleable.

Giannelis is focussing on producing interpenetrating metal-ceramic microstructures using sol-gel processing. In its basic form the process involves dispersing Ni(HCOO)<sub>2</sub> in an alumina sol which is produced by hydrolysis and condensation of aluminum sec-butoxide. After drying the gels are reduced in flowing H<sub>2</sub> at 1000°C followed by hot-pressing at 1350°C under a partial oxygen pressure, p<sub>O<sub>2</sub></sub> = 10<sup>-14</sup>. The nickel salt is added to the alumina sol which eventually leads to a uniform dispersion of Ni in the ceramic matrix. After hot-pressing in a reducing atmosphere, metallic nickel in a densified alumina matrix is produced with the microstructure shown in Fig. 8.

Burlitch is using chemical synthesis techniques for the *in situ* syntheses of Ni-Al<sub>2</sub>O<sub>3</sub> composites, especially through the use of displacement reactions, and for developing new routes for incorporating dopants, especially Cr<sub>2</sub>O<sub>3</sub>, for strengthening the metal-ceramic interface in Ni-Al<sub>2</sub>O<sub>3</sub> composites. One way to prepare metal-ceramic composites *in situ* is to generate the metal by means of an

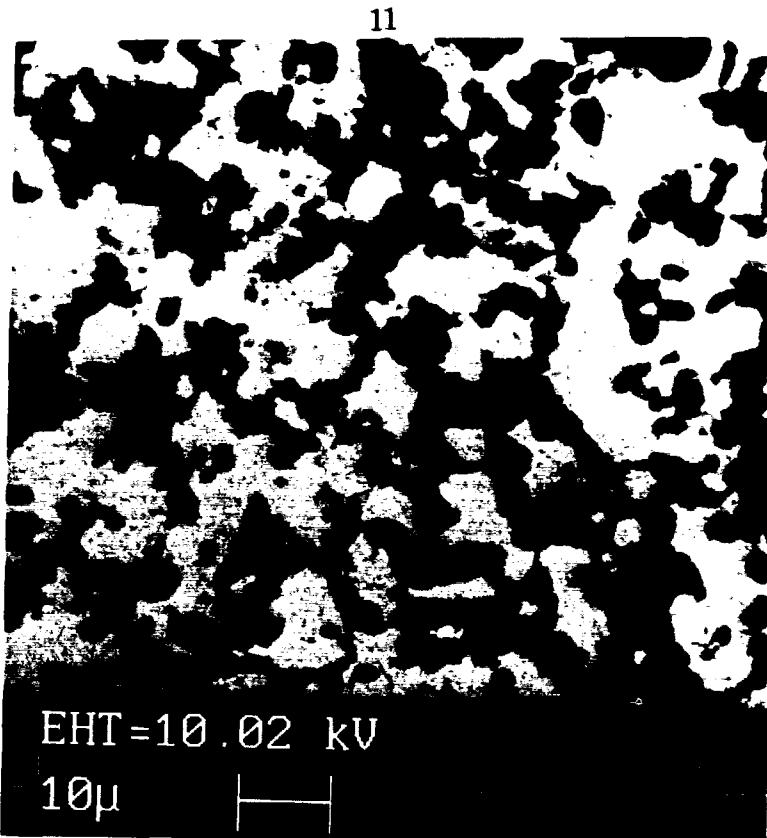
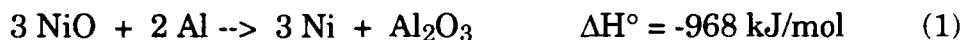


Fig. 8 Illustrating interpenetrating metal-ceramic microstructure produced by sol gel processing.

oxidation-reduction reaction in which the reducing agent is contained within the specimen. Much of the work to produce Ni-Al<sub>2</sub>O<sub>3</sub> composites has focused on displacement reactions between NiO and Al metal powders. Some work has also been done with composites of Ni and Cr-doped Al<sub>2</sub>O<sub>3</sub>.

The equations describing the preparation of Ni-Al<sub>2</sub>O<sub>3</sub> composites (eqn. 1) and NiAl and Al<sub>2</sub>O<sub>3</sub> (eqn. 2) by displacement reactions are:



The microstructures in Fig. 9 are for Ni-Al<sub>2</sub>O<sub>3</sub> and in Fig. 10 are for NiAl-

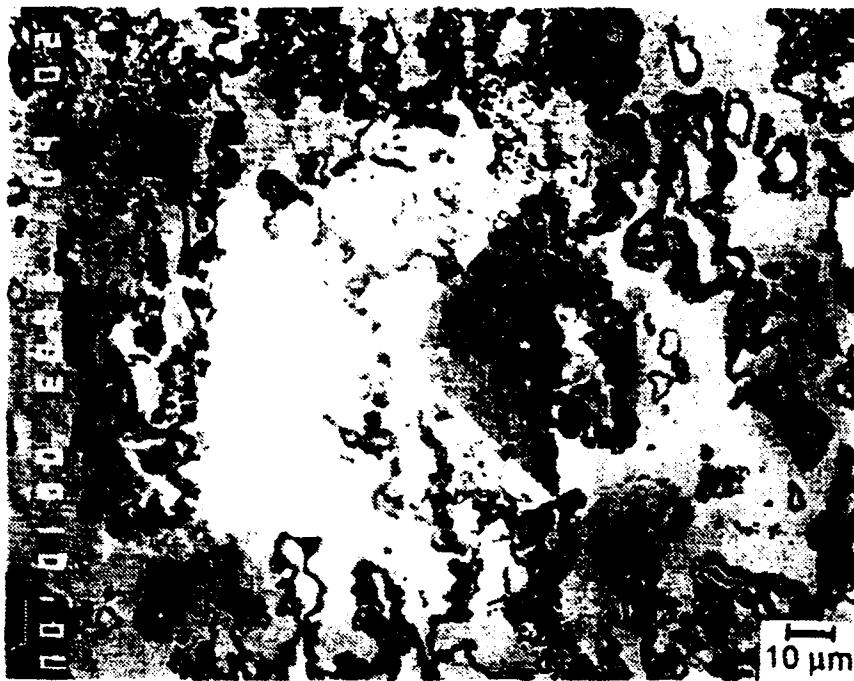


Figure 9 SEM micrograph of a composite of nickel and alumina prepared at 1300°C from NiO and Al.  $\text{Al}_2\text{O}_3$  is medium gray, Ni is lighter gray, and pores are black. The indentation is for a 3 kg load.

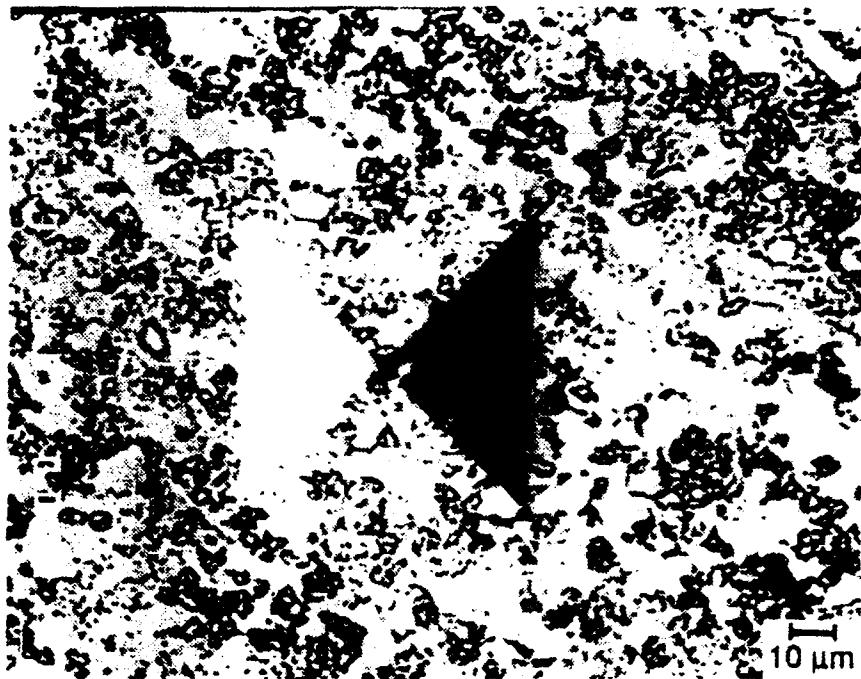


Figure 10 SEM micrograph of a composite of NiAl and  $\text{Al}_2\text{O}_3$  prepared at 1300°C from NiO and Al. The indentation is from a 3 kg load.

$\text{Al}_2\text{O}_3$ . Indentation tests up to a 3 kg load did not form cracks in either microstructures, showing the toughness of the composites.

## 2. Mechanical testing

The interfacial fracture toughness is an important factor in determining the performance of most composite materials. In the case of a ceramic matrix composite with ductile metal particles one wants the interface to be strong so that metal particles will have an opportunity to blunt and to bridge across cracks. With this in mind Zehnder has measured the toughness of the Ni- $\text{Al}_2\text{O}_3$  interface. Test samples were prepared by placing a thin Ni foil between two polycrystalline  $\text{Al}_2\text{O}_3$  blocks and bonding them together under pressure at 1300°C in a low oxygen atmosphere. The resulting fracture toughness of 1 to 3 MPa-m<sup>1/2</sup> (depending on the ratio of tensile to shear stress) is lower than that of  $\text{Al}_2\text{O}_3$  (about 4 MPa-m<sup>1/2</sup>). This result implies that in a ceramic the metal will debond from the ceramic rather than bridging cracks and enhancing fracture toughness. This information is being used by Hui in his calculation of the critical Ni particle size in the presence of thermal stresses.

## 3. Micromechanical Modelling

Hui, Phoenix, Nichols and Zehnder are working on developing basic rules and criteria to optimize the mechanical behavior of *in situ* processed metal-ceramic microstructures operating under high temperature conditions. Analytical and numerical models will be developed to simulate the deformation and fracture properties of these microstructures.

Hui is examining a variety of issues associated with metal-ceramic microstructures, including,

(a) The debonding of Ni particles from  $\text{Al}_2\text{O}_3$  due to thermal stresses

Sass has shown that above a critical diameter Ni particles can be completely debonded from the  $\text{Al}_2\text{O}_3$  matrix due to residual stresses induced by a mismatch in thermal expansion coefficients between Ni and  $\text{Al}_2\text{O}_3$  (see Fig. 3). Hui has

developed a theory to predict the critical particle size below which complete debonding can not occur. A cylindrical particle with an interface crack under thermal loading is shown in Fig. 11. An important result is that, for this system, the energy release rate,  $G$ , is directly proportional to the particle size  $a$ . For a given particle size,  $G$  is a function of interface crack length (in this case, the angle subtended by the interface crack  $2\phi$ ) as shown for the normalized energy release rate,  $G/G_0$ , in Fig. 12. Note that  $G/G_0$  reaches a maximum value at a phase angle of  $\sim 64^\circ$ . Using these results and the experimental data on the interface toughness from Zehnder, Hui estimates that the particle size needed to prevent complete debonding is between 0.3 to 0.9  $\mu\text{m}$ . These calculations agree well with the experimental work of Sass in Fig. 3.

(b) Fracture of  $\text{NiAl}_2\text{O}_4$  grain boundaries during processing

Sass has shown that cracks form along the  $\text{NiAl}_2\text{O}_4$  grain boundaries during the reduction process (see Fig. 5). Hui can explain the formation of these cracks by assuming that the partially reduced grains are subjected to internal stresses due to a spatially inhomogeneous volume change which occurs during the reduction process. He has developed a model which allows the calculation of the internal stresses if the volume and the temperature changes are known.

(c) Time dependent creep behavior of metal matrix composites

The role of broken fibers in the creep of fiber-reinforced composites are being studied using a cylindrical cell model consisting of a single broken fiber and a shell of fiber material embedded in an elastic power-law creeping matrix under longitudinal and transverse loading. The long time creep behavior of the composite is obtained in closed form. It is shown that when a fiber is broken, the increase in the normal stress in the surrounding intact fiber can be significant. Furthermore, applied transverse tension can reduce the composite's creep strain and the normal stress in the fibers.

(d) Modelling the creep strength and fracture toughness of metal matrix composites

Hui has chosen a specific class of microstructures to model the effect of the

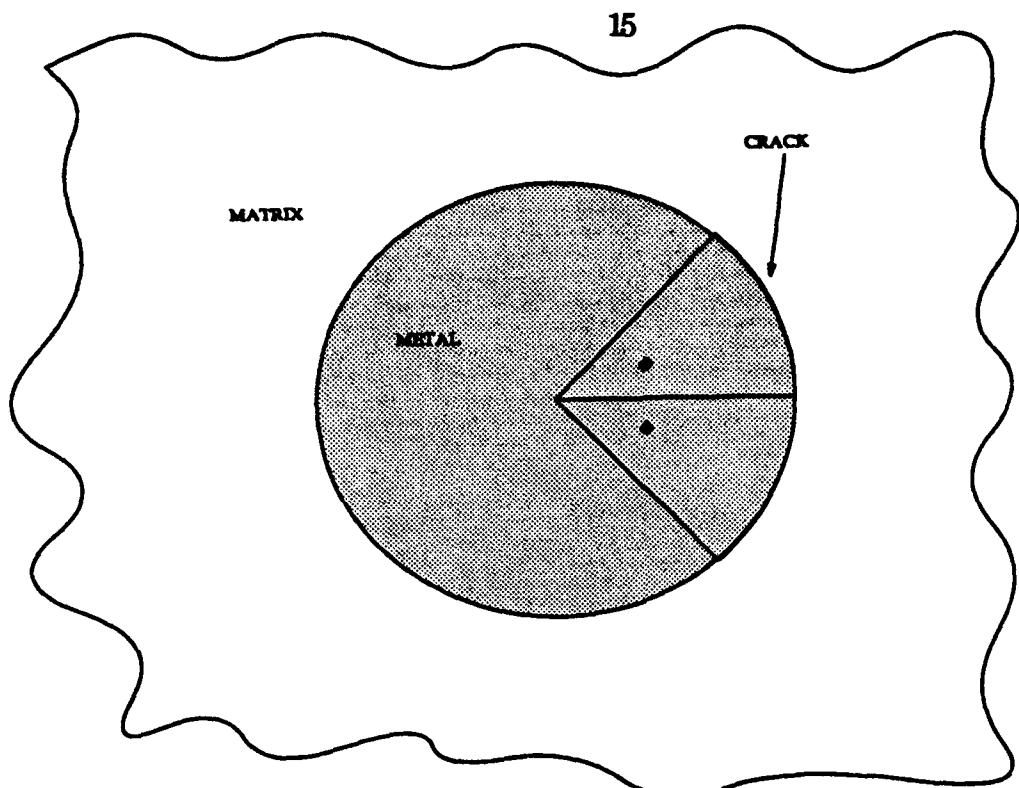


Figure 11 A schematic diagram of the interface crack geometry

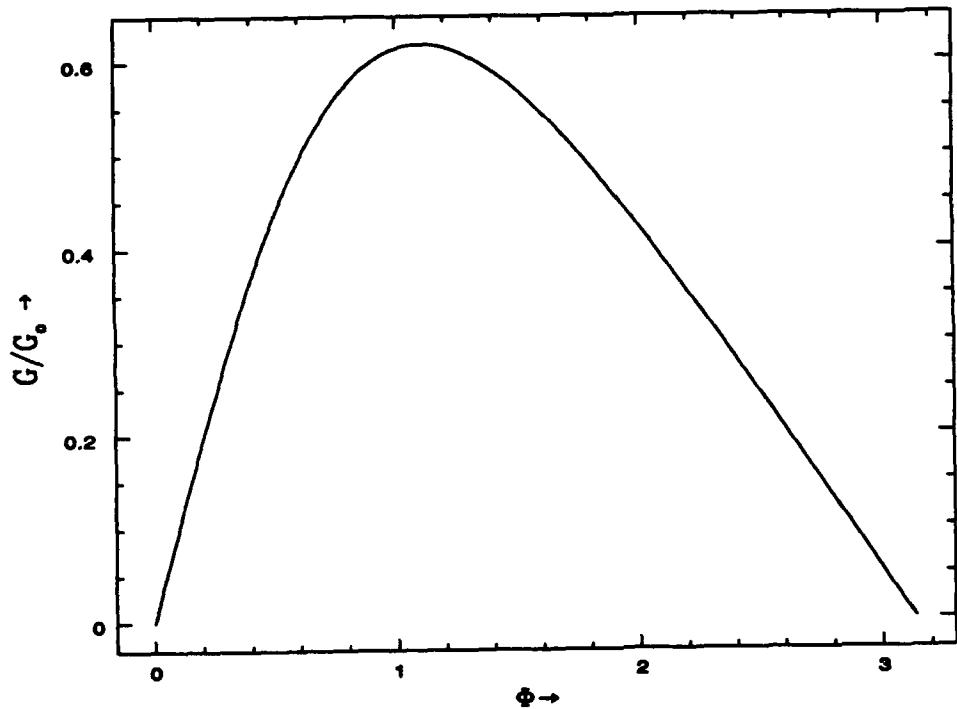


Figure 12 Normalized energy release rate vs. half the angle subtended by the crack.

underlying microstructural parameters on the fracture toughness and the creep strength of a metal matrix composite. In other words, microstructural parameters such as grain size, plastic flow rule of the metal, fracture toughness of the different phases, as well as the interface behavior are the inputs to his model. The microstructure being modelled consists of thin metal layers sandwiched between ceramic grains, one of the typical morphologies produced by *in situ* processing.

Nichols is working on understanding the relationship between mechanical properties such as strength and toughness, and microstructure in composite materials using computer simulations. She has made progress in defining features of model systems, which has allowed her to identify two types of models for further study. In order to model mechanical properties of metal-ceramic composites, model systems must be able to incorporate the following features:

- Any geometrical arrangement of ceramic and metal phases;
- Arbitrary properties of grains, interfaces, and triple junctions;
- Defects such as cracks and microvoids;
- A variety of loading conditions.

In addition, computations to determine the strength, toughness, and yield stress of these models must be efficient and tractable to allow timely acquisition of results from the computer. These considerations led to the choice of two types of models; spring-network models and finite element models.

Spring-network models assume that the properties of grains, interfaces, and triple junctions can be modeled by simple springs and that the material as a whole can be represented by a connected network of springs. Some of the considerations in assigning properties of individual springs include defining the spring constant (or a range of spring constants) and the spring failure stress for all microstructural elements and identifying the yield stress and the spring constant after yielding for the metallic components. Defining a collection of springs that represents faithfully a material with resistance to shear is difficult. The simplest such combination is one in which three springs represent part of two grains and the adjoining interface. Cracks and microvoids are modeled as

the absence of springs, but this simplest model cannot take into account the properties of triple junctions.

Finite element models overcome some of the difficulties of spring-network models. The elements in finite element models also represent microstructural features, but the underlying computational mesh is allowed to vary in complexity as the structure demands. For example, more elements are required to model accurately the properties of triple junctions than are needed for modeling the properties of grain interiors.

For either type of model, the computational demands of determining stress-strain curves are extreme and it therefore is essential to obtain programs which are optimized. Nichols has initiated contact with Liza Monette of Exxon and hope to collaborate in using their spring-network program. ABAQUS will be used for the finite element calculations.

Phoenix is studying the initiation, growth and coalescence of damage that forms wandering crack-like structures, one of which ultimately becomes catastrophic and fails the metal-ceramic material. He is interested in the effect of randomness in the microstructure and local constitutive relations on the overall strength statistics for the material, as well as on fracture mechanics parameters such as toughness. His goal is to put all this into one unified framework. Monte Carlo simulation plays a major role and his goal is to treat system sizes (numbers of fibers, grains) which are two to four orders of magnitude larger than have been treated before in the literature. This advance is necessary to develop fully emerging statistics and fracture features in the material, and requires the development of new analytical techniques beyond the usual finite element or spring network models which tend to be limited to about 50,000 elements. Two types of microstructures are being studied. The first structure involves short, aligned ceramic fibers (also adaptable to platelets) in a metal matrix and is largely unidirectional in its analytical emphasis and focuses on load transfer among elements. The second involves polycrystalline structures involving hexagonal ceramic grains in a metal matrix which forms a thin layer around the grains and where random cracks may form along the interfaces. Damage

initiation begins with distributed randomness introduced at the microstructural level from which emerges localization to form 'cracks' and eventually crack instability. The analytical techniques have much in common for the two systems but exhibit major differences motivated by the very different local geometry.

In the case of the ceramic fibers, the fiber lengths and longitudinal positions are random following Poisson statistics, and fiber strengths follow Weibull/Poisson flaw statistics. The matrix is modelled as elastic/plastic in shear with provisions for possible debonding at critical random shear strains. Also moderate matrix bridging stresses across fiber ends are possible. As the composite is strained in the longitudinal direction fibers begin to fail at random flaws, and debonding also begins to occur around fiber end clusters which occur by chance. Initially the damage is fairly distributed but eventually localization sets in several locations as clusters of failed fibers begin to develop into small wandering cracks. The cracks begin to link transversely and longitudinally to form an unstable catastrophic crack. Over the past year Phoenix has made progress in developing new computational ideas for the problem. They hinge on initially solving basic unit elastic problems which are then used repeatedly in a load transmission factor framework as the damage evolves. Basically the computational work in the algorithms is tied to the amount of damage (fiber breaks, matrix yield and debonding zones) rather than the size of the system. This means that instead of being able to treat a system of say 50,000 fiber, matrix and interface elements which may only have say 500 to 1,000 fiber breaks, he can treat a system of 50,000 fiber failures in any sized system (actually the bigger the better). Thus far he has developed the analytical framework and is now building programs to carry out the computations and simulations for realistic structures and fiber failure arrangements. The algorithms appear powerful enough to make the connection to fracture mechanics quantities for larger arrays of transverse fiber breaks including closing tractions and damage zones ahead of the 'crack' tip.

Phoenix is using the same techniques for polycrystalline structures involving hexagonal ceramic grains joined by thin metal layers. Here he would

like to develop efficient computational schemes for handling random microcrack arrays where the cracks having lengths of the order of many grain facets, not only may meander along interfaces, thus taking sharp turns at grain junctions, but also may interact and link. The computational difficulties are legendary not only for interacting cracks but for kinked cracks. Huge finite element and boundary element programs are typically necessary even to treat very small multiply kinked cracks, much less coupled arrays of such cracks. One of the difficulties involves singularities associated with wedge geometries that develop at grain corners and junctions and these are only partly understood in the literature. A second difficulty involves analytical techniques for crack tips which approach each other at oblique angles. Thus far in the literature, analytical techniques have tended to break down as the tips approach each other. Over the past year he has developed an analytical attack which show promise of handling these cases. Again the approach involves development of 'unit' crack elements with unusual singular behavior ( $1/r$  and  $\log(r)$ ) at their tips which when superimposed under appropriate weighting factors (to be solved for), gives an accurate representation of the full stress field as unwanted singularities cancel. In fact the method appears to work extremely well for aligned arrays of close cracks of random length and becomes exact as the cracks join without giving up the unit features of the joined cracks.

## B. Research Facilities

### 1. Computer System

Zehnder completed installation of the computer system to be used for the micromechanical modelling in January 1994. The system consists of two IBM RS6000 Model 37T workstations, each with 128MB memory, 1GB disk drive and 19" monitors, and four IBM Model 140 X-Stations, each with 17" monitors. The computers are connected to and supported by the Cornell Materials Science Center computing network and are used for a variety of finite element and other simulations.

## **2. Mechanical Testing Facility**

Zehnder is working on developing techniques for performing mechanical properties characterizations of metal-ceramic microstructures at both ambient and elevated temperatures. He is building a facility for measuring fracture toughness, strength, creep rate and other mechanical properties at temperatures up to 1200°C, in controlled atmospheres, on samples as small as 20 mm long. Once data is available on fracture toughness, crack path and creep failure mechanisms, he will work with Hui, Phoenix and Nichols to use these observations as the basis for micromechanical studies of the materials with the goal of developing models that can be used to guide the production of new materials.

Zehnder has completed a preliminary design of the high temperature controlled atmosphere test cell sketched in Fig. 13. Two setups, one for tension testing and the other for bending will be built. For tension testing, flat, side loaded test samples as small as 20 mm long will be used. They are held with the angled grips shown. Due to the very short samples, the grips must be in the hot section of the furnace, thus they will be made of a high temperature superalloy or SiC. Strain will be measured with a capacitive extensometer that has ceramic rods that extend into the hot section. The furnace will be a clamshell type with holes cut into it for extensometer access. To maintain a controlled atmosphere the entire furnace will be surrounded by a gas-tight (but cool) enclosure into which a mixture of nitrogen, carbon monoxide and carbon dioxide will flow. A similar setup will be used for bend testing, except that a bend fixture will be substituted for the grips.

## **3. Processing Laboratory**

A Processing Laboratory is being established within the Department of Materials Science and Engineering, with the financial assistance of the AFOSR/URI grant, the Materials Science Center, the College of Engineering and Cornell University. Three controlled atmosphere furnaces have been designed by Dieckmann and are on order from Germany. A diamond saw was recently

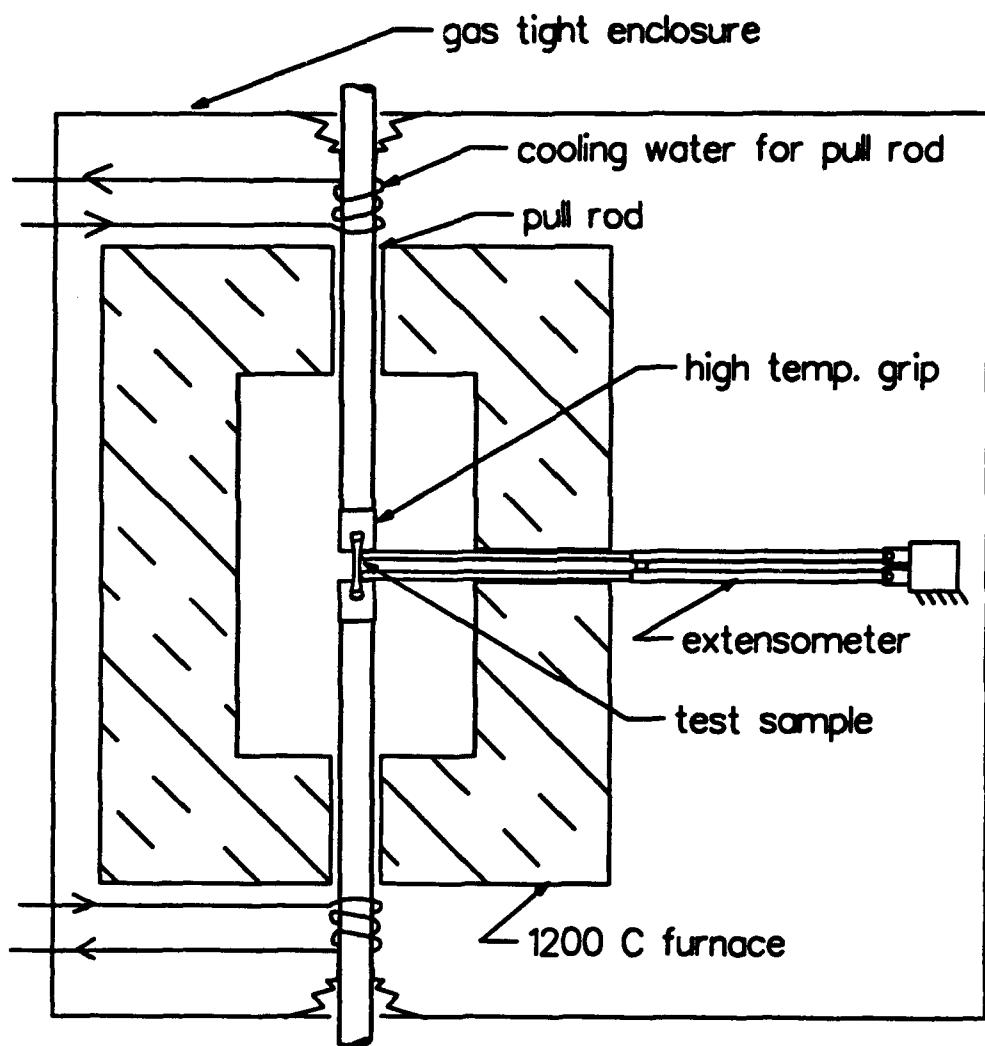


Fig. 13 High temperature controlled atmosphere mechanical testing apparatus.

acquired. Additional slicing, cutting and polishing equipment is available in the Laboratory.

### III. Future Research

#### 1. *In Situ* Processing

Sass will continue work on the Ni-Al-O system, focussing on characterizing the mechanical properties of the Ni-Al<sub>2</sub>O<sub>3</sub> and Ni-defect spinel microstructures formed by reduction reactions, and then varying the reduction conditions in order control the microstructure to achieve the best properties (e.g. highest fracture toughness). He will also study the mechanism whereby small amounts of ZrO<sub>2</sub> suppress cracking due to the large volume change during reduction. The observation that long Ni rods form in a ceramic matrix at 1100°C (Fig. 4(a,b)) will be exploited by carrying out the reduction reaction with a stress applied along one axis of the specimen in an attempt to form a unidirection composite-like array of rods. This could lead to directional reduction reactions.

Dieckmann plans to continue his studies of a variety of reactions that may be useful for forming metal-ceramic microstructures *in situ*. He will perform systematic studies on reactions as a function of different processing parameters. Details of the processes occurring during partial reduction of NiAl<sub>2</sub>O<sub>4</sub> to Ni and Al<sub>2</sub>O<sub>3</sub> (or defect spinel) are not clear at present. Information on the rate determining diffusion process(es) - cationic (Al or Ni) diffusion and/or oxygen diffusion - would be very valuable for a deeper understanding of the reduction process. Cracking was observed as a result of the partial reduction of pure, large-grained NiAl<sub>2</sub>O<sub>4</sub> samples. This must be attributed, at least partly, to volume changes occurring during reduction and possibly also to stresses developed during cooling due to thermal expansion coefficient mismatches. To better understand the contribution of volume changes to crack formation, information on the diffusion of different species would be very valuable.

Initial reactions between Al and single crystal NiO have yielded NiAl<sub>2</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>-rich layers with Al-rich intermetallic phases (Al<sub>3</sub>Ni<sub>2</sub>, Al<sub>3</sub>Ni) dispersed in

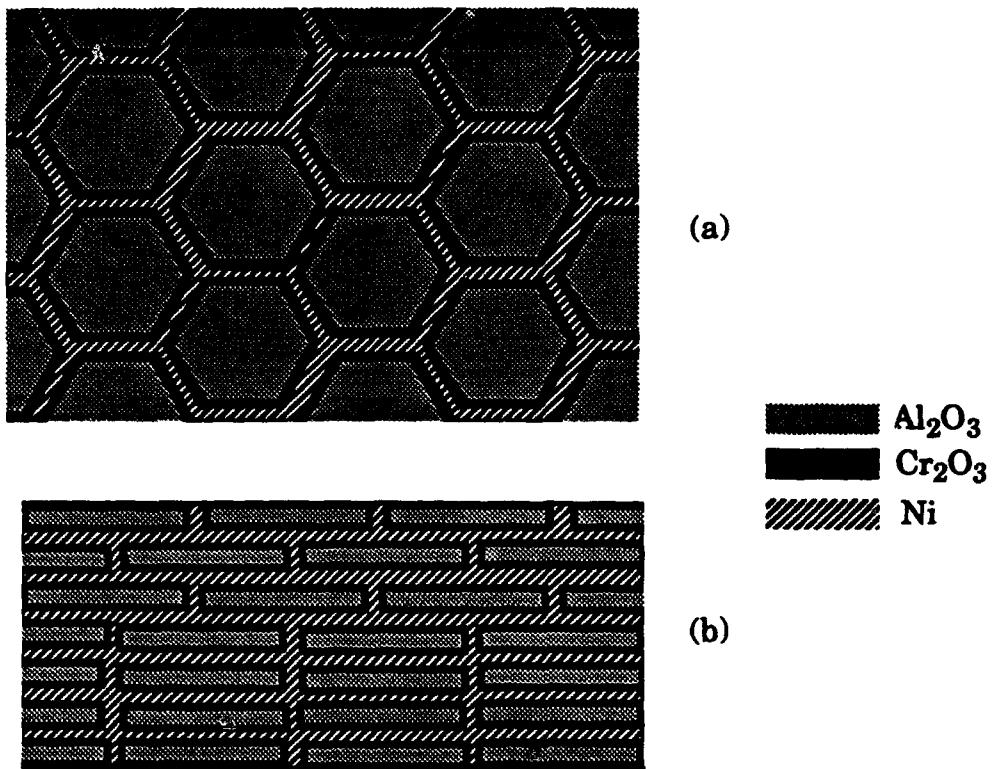
them, and a layer with a combination of Al,  $\text{Al}_3\text{Ni}_2$  and  $\text{Al}_3\text{Ni}$ . Dieckmann plans to perform a systematic study of the rate of formation of these different layers and the various morphologies of the phases. This will give an insight into the possible diffusion pathways and also into the effect of chemical potential gradients of oxygen and the different cationic species. Similar understanding of the reaction between liquid Al and  $\text{NiAl}_2\text{O}_4$  is also needed.

Giannelis will focus on characterization of the interpenetrating  $\text{Ni-Al}_2\text{O}_3$  microstructures, using TEM and mechanical testing including fracture toughness measurements in collaboration with Sass and Zehnder, and then optimization of the composites prepared by sol-gel processing. Emphasis will be placed on domain/grain size and its effect on mechanical properties. In addition, Giannelis, in collaboration with Burlitch, will attempt to control the strength of the metal-ceramic interface by incorporating various dopants that would ultimately lead to optimal mechanical properties.

Burlitch will concentrate on producing specimens by displacement reactions for mechanical testing in collaboration with Sass and Zehnder. The volume fraction of  $\text{Al}_2\text{O}_3$  will be varied by addition of  $\text{Al}_2\text{O}_3$  platelets or powder. The addition of dopants to control interfacial properties will be explored by sol-gel techniques. A study of the dependence of fracture toughness (and other properties) on Ni and Cr content will be conducted. To prepare a rather different, easily modelled  $\text{Ni-Al}_2\text{O}_3$  composite, Burlitch will deposit Ni metal onto single crystalline platelets of  $\text{Al}_2\text{O}_3$ . The idealized microstructure shown in Fig. 14 should allow theoretical modelling of the composite and a correlation of structure to mechanical properties.

## **2. Mechanical testing**

Now that funds for the mechanical test setup have been secured Zehnder will finalize its design and start construction. His goal is to acquire most of the components of the system by the end of the summer 1994 and to spend the fall integrating them into a testing system. Once the setup is completed and tested, he



**Figure 14** Idealized microstructure of composites prepared from nickel coated alumina platelets. (a) top view; (b) cross section showing two possible stacking sequences.

will perform room and high temperature strength and fracture toughness measurements on samples of  $\text{Ni-Al}_2\text{O}_3$  and  $\text{Ni}$ -defect spinel composites made by students of Sass, Giannellis, Dieckmann and Burlitch.

The work on  $\text{Ni-Al}_2\text{O}_3$  bonding will continue with support from the Materials Science Center, with the information used in theoretical modelling calculations performed by Hui. Zehnder will explore bonding at even lower oxygen partial pressures, bonding of single crystal  $\text{Al}_2\text{O}_3$  to  $\text{Ni}$ , and introducing dopants to the interface. He will also explore alternate methods of processing with the goal of decreasing the cost and time needed to prepare and test the samples.

### 3. Micromechanical Modelling

Hui will concentrate on the development of a computational model which will allow the prediction of the fracture toughness and the creep strength of metal matrix composites, assuming a given set of microstructural parameters. The problem is to optimize the creep strength and fracture toughness of the microstructure in Fig. 14 by controlling (a) the interface behavior, (b) geometric factors such as grain size, the thickness of the metal layer, and (c) the flow properties and fracture toughness of the metal and the ceramic grains. In general, crack growth can occur along the metal-ceramic interfaces, in the metal phase and in the ceramic grains. Since the fracture toughness of this composite is primarily controlled by the amount of plastic deformation, it is important to use a realistic model to describe the plastic deformation in the metal layer which can be one micron or less in thickness. The amount of plastic deformation, however, is significantly affected by the local fracture mechanisms, the composite geometry, the interface behavior, and the fracture and flow properties of the metal and the matrix. Large amount of plastic deformation generally leads to a low creep strength but high fracture toughness.

Although this problem is Hui's main focus for this coming year, he will continue to study the debonding of Ni particles in an  $\text{Al}_2\text{O}_3$  matrix. His calculation is based on an isolated particle in an infinite matrix, so that interactions between neighboring particles are unaccounted for. A preliminary calculation indicates that this effect can be significant. He is now extending this calculation to more complicated geometries so that the interaction between particles can be quantified.

Hui will continue his close interaction with the experimental work of Sass, Dieckmann, Giannelis, Burlitch and Zehnder. Such interactions will likely bring in new or unexpected results which we will attempt to quantify with modelling.

Now that Nichols has identified the essential features of any model system and selected two computational strategies for implementing them, next year she will turn to specific studies. In particular, she plans to study three properties: strength, toughness and yield stress. These were chosen because of their

accessibility to computations as well as their overall importance in evaluating the performance of metal-ceramic microstructures. Systems consisting initially of a purely random mixture of ceramic and metal grains *with variable properties themselves* will be constructed within the context of both models and the stress-strain curves calculated. From these curves, she can extract the composite strength, toughness, and yield stress. She will study systems of various sizes and quantify the size-dependence behavior. Disorder in these simple random systems is defined as the range of spring or element properties; e.g., a system with zero disorder consists of identical springs or elements. The results of the two models will be compared.

Once the properties of these simple systems are understood, Nichols will introduce the next level of complexity: assigning properties to the individual interfaces. The mechanical behavior of metal-ceramic interfaces is not well understood. She will use input from continuum calculations of Hui and the fracture toughness measurements from Zehnder in these calculations.

Many metal-ceramic composites do not consist of random arrangements of metal and ceramic grains. Nichols will consider systems containing ceramic grains of large aspect ratios or fibers. This challenge will be met by suitably modifying the spring-network model geometry and the underlying finite element mesh. This phase of the project is of a much longer term nature.

Phoenix will continue to develop computer programs to implement the algorithms developed over the past year for the microstructure involving short, aligned ceramic fibers in a metal matrix. He will then study fracture statistics, size effects and crack growth in several systems whose microstructural parameters mimic those being developed by the *in situ processing* group. He will search for scaling laws and critical values of certain processing and microstructural parameters needed to produce superior strength, reliability and toughness performance. For the case involving polycrystalline structures with hexagonal ceramic grains joined by thin metal layers, Phoenix will continue to investigate the unit crack problems and interaction effects necessary to model a large distributed network of microcracks. Once he gets a reasonably accurate

trial framework set up (tested against known solutions), he will develop a Monte Carlo simulation program building on an initial distribution of interface cracks to model breakdown in material with microstructural parameters representative of those produced by the materials group. By working with increasingly sophisticated unit elements, the procedure shows promise of becoming more and more accurate for a given crack array but at the cost of more computation in the mathematical matrix inversion.

### **Technical Reports**

1. "Growth of Nickel Aluminate Single Crystals by Floating Zone Method", R. Subramanian, M. Higuchi and R. Dieckmann, Submitted for publication (1993)
2. "In Situ Formation of Composites of Alumina with Nickel and With Nickel Aluminide", S. A. Jones and J. M. Burlitch, Submitted for publication (1994)
3. "On Creep of Unidirectional Fiber Composites With Fiber Damage", Y. Song, G. Bao, and C. Y. Hui, Submitted for publication (1994)
4. "Synthesis of Two-Phase Ceramic-Ceramic Microstructures by Precipitation Reactions in the Ni-Al-O System", Z. Zhang, M . Kurosawa and S. L. Sass, Submitted for publication (1994)

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